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Structural Characteristics of Organic/Inorganic Hybrid Gels

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Gelation process and structure of the hybrid organic/inorganic system based on triethoxysilyl terminated polymer (polytetramethylenoxid, PTMO) and tetraethoxysilane (TEOS) prepared in acidic conditions with excess of water were studied by time-resolved synchrotron small-angle X-ray scattering (SAXS). Despite that the rate of gelation process depends strongly on the concentration of acid and the ratio of organic/inorganic components the resulted structure (as revealed by SAXS) was found to be very similar and almost invariant upon gelation. The formation of inorganic clusters was not observed within experimental time, which is probably very slow in the present condition.

KEY WORDS: Hybrid gel/ Small-angle X-ray scattering/ PTMO/ TEOS/ Sol-gel transition

1. INTRODUCTION

Both polymer and inorganic gels are the examples of amorphous systems. Information about the structure of amorphous materials can be provided by electro-magnetic wave scattering in terms of the electron density distribution. Among electro-magnetic waves, the wavelength of X-ray is in the order of 1 Å. Thus the small-angle X-ray scattering (SAXS) affords the information about the density distribution in the range from 5 Å to 1,000 Å, although the range of resolution depends mainly on instrumental conditions. If a powerful source of X-ray is available, the exposition time is reduced enough to be able to observe the structural change of such systems due to phase transition including gelation in real time.

The gelation process is described in general by the formation of a continuous three-dimensional network structure of macroscopic size, despite that the process can be realized in many different ways.

This paper discusses the gelation process and structure of the organic/inorganic system based on triethoxysilyl terminated polymer (polytetramethylenoxid, PTMO) and tetraethoxysilane (TEOS) from the results obtained by time-resolved synchrotron radiation SAXS. The present system is composed of organic (polymer) and inorganic (silicon) parts. Since the gelation process differs in organic and inorganic components, it will be useful to make a brief

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comparison of the gelation mechanism in polymer and silicon systems.

2. GELATION OF TELECHELIC POLYMERS

The polymer used in this study is telechelic. Gelation of telechelic polymers proceeds via reactions of end groups. The simplest example of this case is the system composed of three-branched molecules bearing the end groups of the same kind capable of an addition reaction (Fig. 1). Reaction of two monomers will produce a dimer with four reactive end groups, which react further with a monomer or a dimer to yield a trimer or a tetramer with five or six reactive end groups, respectively. The larger species with increasing number of reactive end groups are being formed progressively. At a certain extent of reaction (gel point), one gigantic molecule of macroscopic scale can be found among other species. Some properties of the reaction system change drastically (the viscosity change is the most noticeable). The mixture acquires elasticity even though containing still a large fraction of lower molecular weight polymers (sol) at this time. Smaller molecules with unreacted groups are further linked together or more frequently to the gigantic molecule (gel) increasing its weight fraction. Many (long) rings will be formed in gel during this process, resulting in the increase of elastic modulus and a very complicated topological structure. At the end of the process the prevailing part of initial reaction mixture is incorporated in gel.

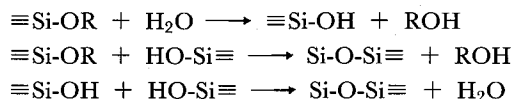
In order to compensate a small choice of reactive groups capable of mutual addition (or condensation) reaction, (linear or branched) telechelic polymers are in practice reacted with a low molecular weight (linking agent) having different types of reactive groups. The condition for gelation is the same as for the polyaddition (polycondensation) of multi-functional monomers as first formulated by Flory.¹⁾ The gel point is given for the random f -functional polycondensation in terms of the conversion of functional groups α as

$$\alpha_c = 1/(f-1) \quad (1)$$

where α_c denotes the critical conversion and gel is formed when α exceeds α_c . If the reaction system is not too dilute and the length of polymer arms is long enough, this condition is well fulfilled by telechelic polymers.

3. GELATION OF ALKOXYSILANE

The end groups of polymers used in this study could be regarded as substituted alkoxyxilanes. Gelation of alkoxyxilanes proceeds in a different way from that of telechelic polymers. At the beginning of the reaction alkoxyxil groups are hydrolyzed to form silanol groups which condensate to siloxane bonds by releasing water and alcohol:



In this scheme shown above, it would seem that the condensation of silanol groups leads to the formation of more branched molecules and finally forms gel in the way similar to multi-functional polycondensation. In reality, gel is formed but the gel structure and gelling mechanism are completely different from simple polycondensation (Fig. 1b). According to

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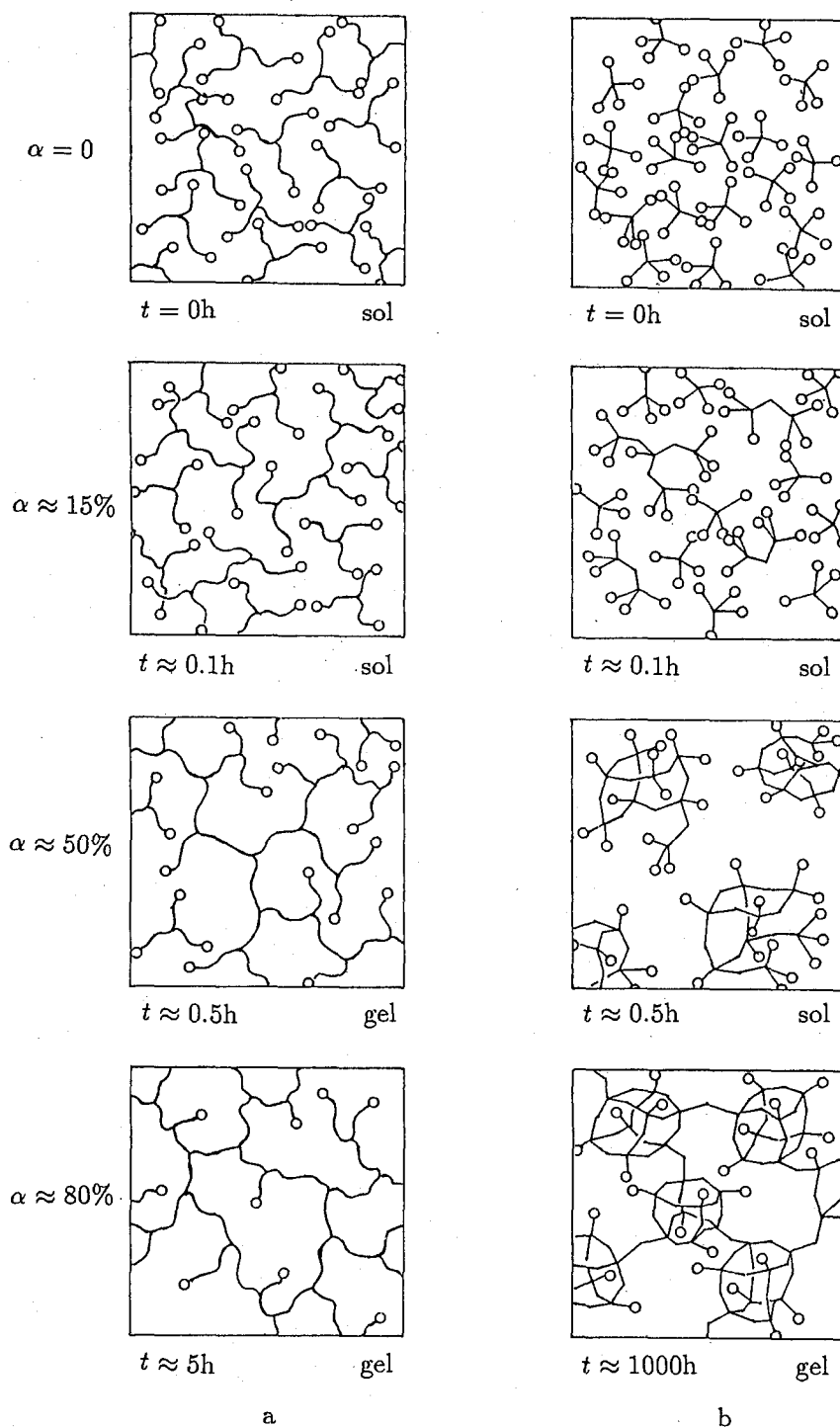


Fig. 1. Schematic view of gelation process of (a) telechelic polymer and (b) alkoxyasilanes (in acidic condition assuming complete hydrolysis of alkoxyisilyl groups). The sketches are given in two different space scales.

ller,²⁾ polycondensation of silanols occurs in three stages of (i) polymerization of monomer to form particles, (ii) growth of particles, and (iii) linking of particles into chains and network which extends throughout liquid medium, and thickening to gel.

Since the environment will change during reaction in a close proximity of reacting groups, the reactivity of the groups becomes much sensitive to the type of neighbour substituents and the presence of ions (H^+ , OH^- , F^- , etc.) in reaction mixture. The consequence is seen in the tendency to form small (three- or four-membered) rings of siloxane bonds (if hydrolysis is much faster than condensation) and the (de)protonization of silanol group depending on pH. All those factors promotes the formation of small particles in the early stage of reaction. The size of particles depends on the reaction condition. In the final stage, the particles aggregate into a gel state.

If the gelation of TEOS proceeds with random condensation, the gel point is given by

$$p_{crit} = 1/3 \quad (2)$$

where p is the probability that either alkoxyisilyl or silanol group on a silicon atom is reacted to form the siloxane link and the subscript *crit* denotes the critical (gel) point. It is known that in practice the critical probability for gelation of TEOS is much higher when gelation takes place exclusively via covalent bonds, and the condition given by eq. (2) is never fulfilled.

4. GELATION OF TRIETHOXYISILYL-TERMINATED POLYMERS

The gelation process in the present system is expected to be characterized in terms of two gelation processes outlined in the sections 2 and 3. Here polymer chains are endlinked by hydrolysis of triethoxysilyl groups and subsequent condensation of silanol groups. Silanol groups self-condensate to form siloxane bonds as described in the section 3.

Assuming a random reaction, the gelation of the present system can be formulated in a similar way as the two cases described in the sections 2 and 3. If no TEOS participates in reaction, the gel point is given by

$$p_{crit} = 1/5 \quad (3)$$

where p is the probability that either alkoxyisilyl or silanol group on a silicon atom reacted to form a siloxane link. If we consider only the inorganic components (triethoxysilyl end groups), an infinite siloxane network will be formed when the condition

$$p > p_{crit}^{inorg} = 1/2 \quad (4)2$$

is fulfilled. That is, if the reaction is completely random, an organic infinite network is formed at first and then an inorganic network is incorporated in the present system as the reaction proceeds.

When some TEOS is added, the corresponding gel points are given as

$$p_{crit} = \frac{3r+2}{15r+6} \quad (5)$$

$$p_{crit}^{inorg} = \frac{3r+2}{6r+6} \quad (6)$$

where r denotes the molar ratio of polymer to TEOS. The condition given by eq. (5) could be

fulfilled if the reaction system is not too dilute and the polymer chain is long enough. The formation of an infinite inorganic network may take place in a similar way as described in the section 3 for a pure alkoxysilane system.

5. EXPERIMENTAL

5.1. Materials

Linear triethoxysilyl terminated poly(tetramethyleneoxid) ($M_n=1,350 \text{ g}\cdot\text{mol}^{-1}$) and TEOS were reacted in ethanol/water mixture with hydrochloric acid as a catalyst. Two series of samples were prepared, where the initial molar ratio of a total amount of ethoxysilyl groups, water and ethanol was fixed as

$$[(\text{Si})-\text{OEt}]_{\text{tot}} : [\text{H}_2\text{O}] : [\text{EtOH}] = 3 : 20 : 20$$

for all samples.

Series I were prepared without adding TEOS, where the catalyst amount varied as shown in Table 1. Series II contains some amount of TEOS in such a way where the total concentration of ethoxysilyl groups was kept constant (see Table 2). Thus the initial composition of ethoxysilyl groups, water and ethanol is the same as in Series I, and the catalyst amount $[\text{HCl}]$ was fixed to 0.18 in terms of the molar ratio.

The samples were prepared in 5 ml bottles. Polymer, ethanol, and water were mixed with or without TEOS, stirred intensively by an electromagnetic stirrer at 20°C for 5 min. Then the catalyst was added and the reaction mixture was stirred at 20°C for further 3 min.

Gelation times were determined by observing the viscosity of the samples (by tilting the bottles).

Table 1. Initial composition and gelation times of the samples in Series I.

Sample	$[(\text{Si})-\text{OEt}]_{\text{P}} : [\text{H}_2\text{O}] : [\text{EtOH}] : [\text{HCl}]^{\text{a}}$				$w_{\text{P}}^{\text{b)}$	w_{EtOH}	$w_{\text{H}_2\text{O}}$	t_{g} , min
SG11	0.36							10
SG1	0.24							17
SG2	0.18							21
SG3	3	20	20	0.12	0.35	0.47	0.18	30
SG4	0.06							60
SG5	0.03							110
SG12	0.015							270
SG0	0							—

a) initial molar ratio, b) weight fraction.

Table 2. Initial composition and gelation times of the samples in Series II.

Sample	$[(\text{Si})-\text{OEt}]_{\text{P}} : [(\text{Si})-\text{OEt}]_{\text{T}} : [\text{H}_2\text{O}] : [\text{EtOH}] : [\text{HCl}]$					w_{P}	w_{T}	w_{EtOH}	$w_{\text{H}_2\text{O}}$	t_{g} , min
(SG2)	3.0	0				0.35	0	0.47	0.18	21
SG6	2.7	0.3	20	20	0.18	0.32	0.01	0.48	0.19	28
SG7	2.4	0.6				0.29	0.02	0.50	0.19	40
SG8	2.1	0.9				0.26	0.03	0.51	0.20	54

5.2. Instrumentation

The small-angle X-ray scattering (SAXS) measurements were performed with an SAXES optics installed at BL-10C of the Photon Factory, Tsukuba. The time-resolved SAXS was observed from the reaction mixture undergoing gelation, using a cell holder described previously³⁾ The reaction mixture was put into a glass capillary of a diameter of 2 mm and inserted into a temperature-controlled heat block. The SAXS measurements were started immediately after inserting the capillary cell filled with the reaction mixture. The temperature during SAXS measurements was maintained at 50°C for Series I and II. Two-minute SAXS measurements were repeated with an appropriate time interval over 60 to 120 mins. for the samples SG1 to SG12. SAXS from SG0 was accumulated for 10 minutes, but not repeated.

The scattering intensities were corrected with respect to the background scattering and the absorption of the samples.

6. RESULTS AND DISCUSSION

The scattering intensity $I(q)$ from a volume of an homogeneous amorphous material can be expressed in terms of a correlation function (of electron density fluctuation) γ as⁴⁾

$$I(q) \propto \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin qr}{qr} dr \quad (7)$$

where $q = (4\pi/\lambda) \sin(\theta/2)$ is the magnitude of the scattering vector with λ and θ being the wavelength and the scattering angle, respectively. $\gamma(r)$ is defined as the average of the product of two fluctuations in electron density $\Delta\rho(\mathbf{r})$ at two positions \mathbf{r}_1 and \mathbf{r}_2 at a distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$:

$$\gamma(r) = \langle \Delta\rho(\mathbf{r}_1) \Delta\rho(\mathbf{r}_2) \rangle \quad (8)$$

The average is taken over all directions of the vector $\mathbf{r}_1 - \mathbf{r}_2$.

Various correlation functions have been proposed to describe scattering patterns.⁵⁾ It should be noted that most of those correlation functions can be incorporated in the general description for the assembly of independent domains characterized by the fractal dimension D where the density correlation is assumed to decay as r^{D-d} with a distance r in the d -dimensional space.⁶⁾ Correlation functions of three kinds (Lorentzian, Gaussian and Debye-Bueche type) are often used. They are summarized in Table 3 with corresponding intensity functions. Here numerical multipliers are omitted, and ξ , ξ_G and a are the *correlation lengths* which measure the density decay in the region.

Due to a linearity of Fourier transformation, any linear combination of correlation functions will be transformed into a linear combination of corresponding scattering intensities. The decomposition into Gaussian in lower and Debye-Bueche term in higher q -region:

$$I(q) = I_G(0) \exp(-\xi_G^2 q^2/2) + \frac{I_{DB}(0)}{(1+a^2 q^2)^2} \quad (9)$$

Table 3. Correlation functions and scattering intensities.

Type	Correlation function	Scattering intensity
Lorentzian	$(\xi/r) \exp(-r/\xi)$	$\xi^3/(1+\xi^2 q^2)$
Gaussian	$\exp(-r^2/(2\xi_G^2))$	$\exp(-\xi_G^2 q^2/2)$
Debye-Bueche	$\exp(-r/a)$	$a^3/(1+a^2 q^2)^2$

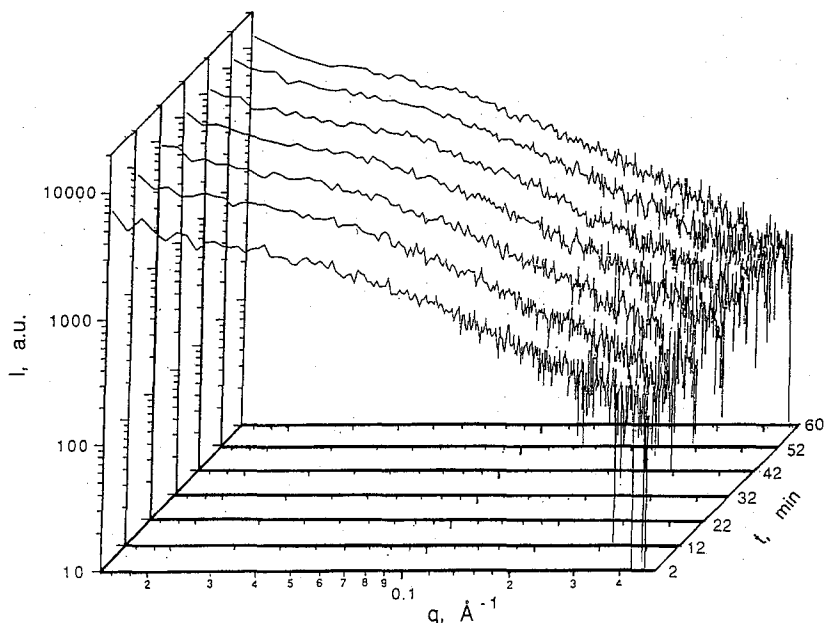


Fig. 2. SAXS profiles for SG1 as a function of time.

was found to fit the observed scattering profiles.

Fig. 2 shows the SAXS profiles of the sample SG1 as a typical example in a double logarithmic scale. Scattering intensities from the samples SG1 to SG12 were found to increase monotonously with time without any manifestation of approaching to a final state. Gel should have been formed in early stages of reaction as deduced from Table 2. Here the structure formation of the system is considered as not yet completed. Thus gel at this stage consists of an infinite network composed of PTMO chains, but still contains a high amount of reactive groups capable of further reaction to lead eventually to the inorganic infinite network.

Rodrigues et al.⁷⁾ investigated the structure of the hybrid gel formed by the reaction of TEOS, ET-PTMO and water with HCl as catalyst in dimethylformamid/isopropanol or tetrahydrofuran/isopropanol as solvent. Since a large amount of TEOS was used, the inorganic particles are formed to yield a well-defined domain which exhibits surface or mass fractal behaviour of silicate particles.⁸⁾

The present system has not matured enough to form a well-defined inorganic domain as confirmed from the analysis by decomposing the scattering profiles into two terms of Gaussian and Debye-Bueche-type (see the discussion below). Thus the fractal behaviour was not observed in particular and the slope (approximately -1) of the scattering curves (Fig. 2) seems to reflect randomly distributed point-like scatterers which may grow into the domains in later stages of reaction.

Scattering profiles of all the samples are found to be represented by two-component functions (see Fig. 3). Two correlation lengths were evaluated accordingly, suggesting the presence of two distinguishable phases characterized by electron density fluctuations in two different space scales. When the Gaussian term and the Debye-Bueche term are applied to the decomposition of the scattering profiles in lower and higher q -regions, respectively, the corresponding correlation

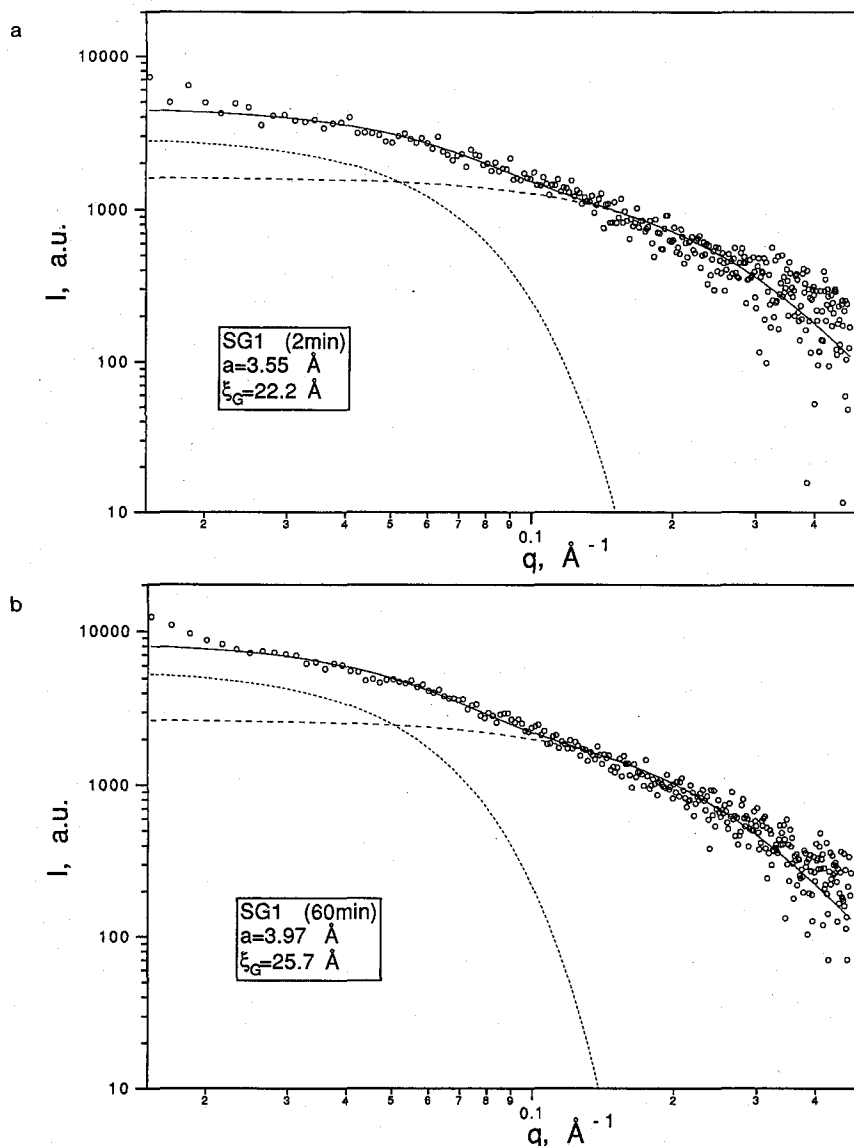


Fig. 3. Decomposition of scattering profiles into Debye-Bueche (---) and Gaussian (.....) parts; (a) 2 min. and (b) 60 min. after reaction started.

lengths are evaluated to be approximately 20 to 25 \AA for the Gaussian correlation length ξ_G and 2 to 5 \AA for the Debye-Bueche correlation length a . The results of the decomposition analysis are summarized in Figs. 4 and 5. In the case of the sample SG0 (prepared without HCl), the values of ξ_G and a are evaluated to be 40 \AA and 9 \AA , respectively. Since the accuracy of the ξ_G determination is sensitive to the experimental errors in the region of the lowest q values, the scattering intensities in the range of $q < 0.02 \text{\AA}^{-1}$ were disregarded in the above analysis.

Both correlation lengths are almost invariant with reaction time. The value of a is as small as several \AA 's, and is considered to correspond to the silicate crosslinks. As seen from Fig. 4b,

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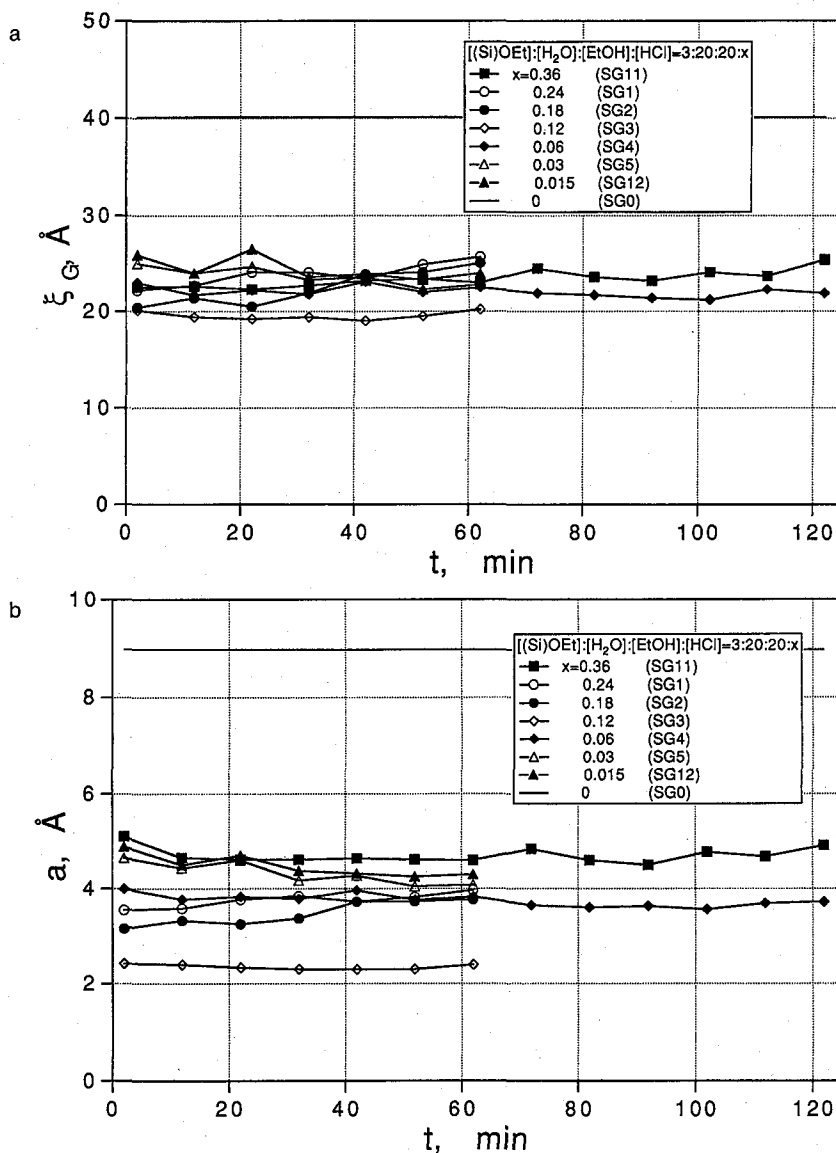


Fig. 4. Time-dependence of correlation lengths evaluated for Series I; (a) the Gaussian correlation length ξ_G and (b) the Debye-Bueche correlation length a .

the a value depends on the catalyst concentration, where a takes a minimum value of 2.3 Å at $C_{\text{HCl}}=5.4 \times 10^{-2} \text{ mol.L}^{-1}$ (SG3, $x=0.12$) which might correspond to an isoelectric point.²⁾ It is well known that the particle size of alkoxyasilanes depends on pH.²⁾ However, the polymer chain was long enough to prevent the further growth of silane particles. The presence of TEOS was found to have no effect on the value of a (Fig. 5b). Thus the silicate crosslinks seem to be composed of at most a few silanol groups.

The Gaussian correlation length ξ_G is much less sensitive to the composition of the systems,

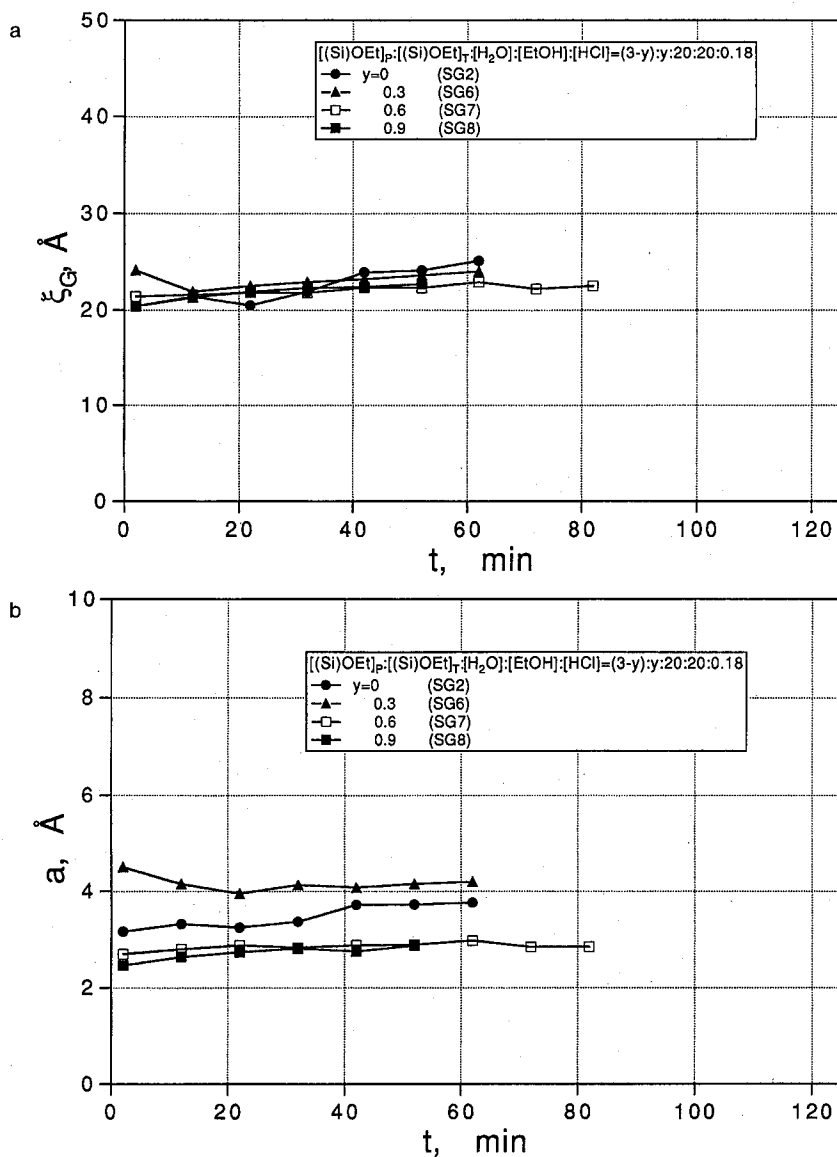


Fig. 5. Time-dependence of correlation lengths evaluated for Series II; (a) the Gaussian correlation length ξ_G and (b) the Debye-Bueche correlation length a .

and lies in the range of 20 Å to 26 Å. The ξ_G value depends slightly on the catalyst concentration but not on the TEOS concentration (see Figs. 5a and 6a). ξ_G takes again a minimum value of 20 Å at $C_{\text{HCl}} = 5.4 \times 10^{-2} \text{ mol.L}^{-1}$ (SG3), suggesting ξ_G also reflects the inorganic domain composed of silicates. Rodrigues et al.⁷⁾ evaluated the radius of gyration of inorganic-rich regions in TEOS/PTMO ceramers which increased from 18 Å to 28 Å over 2 weeks.

We have not observed the growth of ξ_G with time, but the network structure may require much longer time to mature in the present hybrid system.

The results of the analysis is consistent with a general morphological model for metal alkoxide/PTMO ceramers proposed by Rodrigues et al.,⁷⁾ which is composed of three generalized phases of the organic-rich, organic-inorganic-mixed and inorganic-rich regimes. ξ_G and a are considered to represent the inorganic-rich regions and the regions in which the organic and inorganic components are mixed, respectively. The scattering from organic components is apparently suppressed because of the contrast (a large density difference between organic and inorganic components).

7. CONCLUDING REMARKS

Although the formation of hybrid organic/inorganic network prepared under acidic condition depends strongly on the composition of organic polymer and TEOS, the resulted structure was found to be similar as shown by the SAXS profiles. The SAXS profiles are almost invariant upon gelation. Thus it is concluded that the network formation by organic components would not induce any particular structural change in inorganic-rich regions. The network contains a large amount of unreacted silanol groups, which eventually form inorganic clusters. The cluster formation is slow in the organic network medium.

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